

(12) UK Patent Application (19) GB (11) 2 326 165 (13) A

(43) Date of Printing by UK Office 16.12.1998

(21) Application No 9818099.5

(22) Date of Filing 21.02.1997

(30) Priority Data

(31) PN8203 (32) 21.02.1996 (33) AU

(86) International Application Data

PCT/AU97/00101 En 21.02.1997

(87) International Publication Data

WO97/31034 En 28.08.1997

(71) Applicant(s)

Commonwealth Scientific and Industrial Research
Organization
(Incorporated in Australia)
Limestone Avenue, Campbell,
Australian Capital Territory 2601, Australia

(72) Inventor(s)

Jonathan Howard Hodgkin
Hans Jorg Griesser
Thomas Reinhold Gengenbach

(51) INT CL⁶

C08F 2/52, C08J 7/04 7/18

(52) UK CL (Edition P)

C3P PKN
C3R RPX R35PX
C3T TPH T402 T422
C3W W100 W220 W225 W303 W312
U1S S1389 S1559 S1577 S1632 S3042

(56) Documents Cited by ISA

EP 0176636 A1 WO 91/16378 A WO 89/11500 A
AU 910073964 A JP 058008517 A JP 002022339 A
US 5494712 A

(58) Field of Search by ISA

INT CL⁶ C08F 2/52, C08J 7/04 7/18
AU:IPC as above

(74) Agent and/or Address for Service

Elkington and Fife
Prospect House, 8 Pembroke Road, SEVENOAKS,
Kent, TN13 1XR, United Kingdom

(54) Abstract Title

Method for reducing crazing in a plastics material

(57) A method for reducing crazing in a plastics material characterised in that it comprises the steps of: (1) cleaning the surface of the material; and (2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.

GB 2 326 165 /



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 2/52, C08J 7/04, 7/18	A1	(11) International Publication Number: WO 97/31034 (43) International Publication Date: 28 August 1997 (28.08.97)
(21) International Application Number: PCT/AU97/00101 (22) International Filing Date: 21 February 1997 (21.02.97) (30) Priority Data: PN 8203 21 February 1996 (21.02.96) AU (71) Applicant (for all designated States except US): COMMON-WEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION [AU/AU]; Limestone Avenue, Campbell, ACT 2601 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): HODGKIN, Jonathan, Howard [AU/AU]; 28 Celia Street, Burwood, VIC 3125 (AU). GRIESSER, Hans, Jorg [AU/AU]; 20 View Road, The Patch, VIC 3792 (AU). GENGENBACH, Thomas, Reinhold [DE/AU]; 3 Mount Street, Glen Waverley, VIC 3150 (AU). (74) Agents: CORBETT, Terence, G. et al.; Davies Collison Cave, 1 Little Collins Street, Melbourne, VIC 3000 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR REDUCING CRAZING IN A PLASTICS MATERIAL (57) Abstract A method for reducing crazing in a plastics material characterised in that it comprises the steps of: (1) cleaning the surface of the material; and (2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

METHOD FOR REDUCING CRAZING IN A PLASTICS MATERIAL

The present invention relates to a method for reducing crazing in a plastics material, in particular a transparent plastics material.

5

When transparent plastics materials are used for windows, roofing, signs or light fittings maintenance of their original optical clarity is important. Unfortunately, under the influence of environmental factors such as light, heat and moisture many plastics materials suffer from crazing. Crazing is a phenomenon where microvoids form in the body of the materials. These microvoids may not cause a significant deterioration in mechanical strength of the article, but they do reflect/refract light and decrease the clarity of the article. Ultimately, crazing decreases the strength of the article and can lead to failure.

As crazing is a visually obvious deterioration in the material, it gives an impression of poor quality or lack of maintenance which is particularly objectionable in applications where visual clarity is desired. Such applications include the windows of transport vehicles, roofing sheets, light fittings or signs. Many signs are made of transparent materials with the graphic material applied to the underside to be viewed through the material. Crazing in vehicle windows interferes with the vision of the occupants decreasing their enjoyment of the journey and may even pose a real safety hazard. Crazing is particularly objectionable in aircraft windows and frequently causes the replacement, at a great expense, of windows which are otherwise sound and serviceable. As a consequence of the crazing problem, the use of glass windows is being considered for aircraft despite the weight penalty that this would impose.

25 The cause of crazing is unknown and may be manifold. It is thought that one cause is the diffusion of small molecules such as water or surfactants into the material which decreases the attractive forces between polymer chains and allows movement of molecules under internal or external stress thus forming microvoids.

30 According to the present invention there is provided a method for reducing crazing in a plastics material which comprises the steps of:

- (1) cleaning the surface of the material; and

(2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.

The method of the present invention may be used to reduce crazing in a wide variety of plastics materials, such as, for example, acrylics, styrenes, polycarbonates, polyesters or polyurethanes. The plastics material may be an article which is preferably in the form of a laminate or sheet. The method will have particular value when applied to transparent plastics material where visual clarity is important. Examples of transparent materials include acrylic or polycarbonate sheets as used for the windows of transport vehicles such as aircraft, boats, trains and motor vehicles, signs or for architectural uses such as in roofing, glazing sheets and light fittings.

The material may be cleaned in step (1) by any method which leaves the surface substantially free of any contamination capable of interfering with the adhesion of the polymer coating. A preferred method of cleaning the surface is to subject the material to a low pressure plasma of an inert gas such as argon, neon, or nitrogen. Another preferred method of cleaning the surface involves subjecting the material to a low pressure plasma of an oxidising gas such as air or oxygen. Water vapour is also a suitable oxidising gas for this purpose. These cleaning methods may be advantageously carried out in the same apparatus which is used in step (2) of the method.

The monomer used in step (2) may be any saturated or unsaturated organic compound capable of producing a coating of a substantially non-oxidising polymer containing organic groups.

Suitable saturated monomers include siloxanes, fluorinated compounds, lower hydrocarbons, lower alcohols, lower alkylamines and mixtures thereof. The term "lower" as used herein refers to monomers containing 1 to 12 carbon atoms.

Suitable unsaturated monomers include acrylic esters, methacrylic esters, vinyl esters, vinyl aromatics, unsaturated or polyunsaturated hydrocarbons and mixtures thereof. Examples of these monomers include methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate,

methacrylate, ethyl methacrylate, *n*-butyl methacrylate, 2-ethylhexyl methacrylate, vinyl acetate, styrene, *p*-chloromethylstyrene, 2-vinylpyridine, 4-vinylpyridine, N-vinylpyrrolidone, vinyl halides of the formula $\text{CH}_2=\text{CHX}$ wherein X is Cl or F, vinylidene halides of the formula $\text{CH}_2=\text{CX}_2$ wherein X is independently Cl or F, vinyl ethers of the formula $\text{CH}_2=\text{CHOR}$ wherein R is alkyl, and allyl derivatives such as allyl ethers, allyl carbonates or diallyl carbonates.

Plasma polymers from some of these monomer classes typically undergo extensive oxidation on aging (Gegenbach *et al*, *J Polymer Sci, Part A Polymer Chemistry*, **32**, 1399-1414 (1994); Gegenbach *et al*, *Surface Interface Analysis*, in press 1996). In those cases it is necessary to carefully adjust the plasma deposition parameters until minimal oxidation following ageing in the air is obtained. While substantial oxidation can occur in plasma polymers without affecting their structural integrity, minimal oxidation lessens the danger of adverse changes to the surface or mechanical properties of a plasma polymer as it ages. As used herein, the term "substantially non-oxidising polymer" refers to materials which show such minimal oxidation.

15

It has been found that for windows made from acrylic polymers such as those used in aircraft, the substantially non-oxidising polymer coating is preferably hydrophobic. Siloxanes or perfluorinated compounds are particularly suitable monomers for producing hydrophobic coatings provided that the resulting polymer contains some organic groups. Examples of such monomers include hexamethyldisiloxane, vinyltrimethoxysilane, perfluorocyclohexane and tetrafluoroethylene.

For plastics materials where the crazing is caused by exposure to hydrophobic molecules such as petroleum products, a hydrophilic coating may be more suitable in which case monomers such as alcohols or alkylamines may be used. Preferred examples of such monomers include methanol, ethanol and the various isomers of propanol or butanol.

25

The plasma polymer coatings produced by the method of this invention are usually highly crosslinked and hence stable. They may also be abrasion resistant.

30

Many of the materials to which the method of the present invention can be applied are subject to varying stresses in service and move or flex slightly as a consequence. Accordingly,

there is a need to match the mechanical compliance of the coating with that of the material. The present invention achieves this by ensuring that the plasma polymer coating applied in step (2) is thin and adheres well to the material so that it moves with the material without itself cracking or crazing. It is preferred that the plasma polymer coating has a thickness of about 2 to about 5 500 nm, more preferably about 5 to about 50 nm.

The prior art methods produce thicker coatings which are unable to follow the movement of the material and crack and/or delaminate.

10 The method of the present invention may be carried out in any suitable apparatus for performing plasma polymerisation such as that described in AU 654131. AU 654131 describes a process for plasma coating polymeric materials in a vapour of an amide monomer so as to provide a coating suitable for the growth of cells on biomedical implants to be administered into the human body. Preferably, low pressure plasma polymerisation is employed in which the 15 pressure is about 0.5 to about 1.0 torr.

The present invention also provides a craze resistant article comprising a plastics material having a thin coating of a substantially non-oxidizing plasma polymer containing organic groups.

20 This invention is further explained and illustrated in the following non-limiting examples.

Example 1 - Coating of acrylic plastic sheet

Test strips of 35 cm x 3 cm were cut from a 3 mm thick acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues and repeated twice further with fresh tissues. The final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

0.55 Torr pressure of air
225 kHz frequency
10 Watt load power
60 secs duration.

The coating was applied to the air plasma cleaned sample by exposure to a plasma in hexamethyl disiloxane vapour under the following conditions:

0.11 Torr pressure
225 kHz frequency
50 Watt load power
240 secs duration.

A strong adherent coating of plasma polymer was formed.

Example 2 - Evaluation of effect of coatings on craze resistance

Test strips prepared according to Example 1 were tested for susceptibility to crazing using a modification of the cantilever test method of Burchill, Mathys and Stacewicz (*J. Materials Science* **22**, 483-487 (1987)) which is a modification of the standard test method ANSI/ASTM F484-77 "Stress crazing of acrylic plastics in contact with liquid or semi-liquid compounds". The samples were 35 cm long. A weight of 1 kg was suspended from the unsupported end of the test strip. The load was applied for 10 mins before placing the test fluid (iso-propanol) on the tensile surface which was kept wet until examination for crazing (at least a further 20 mins).

Uncoated control strips cut from the same sheet crazed within 20 mins. However, the strips prepared in Example 1 did not craze after 6 hrs when the test was halted.

**EXAMPLE 3 - Coating of Commercial Acrylic Sheet with n-heptylamine polymer after
5 air plasma cleaning**

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an
10 air plasma under the following conditions:

0.50 Torr pressure
200 kHz frequency
10 Watt load power
15 60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-heptylamine vapour under the following conditions:

20 0.40 Torr pressure
200 kHz frequency
10 Watt load power
180 second duration.

25 A coating of plasma polymer ca 120 nm thick formed.

**EXAMPLE 4 - Coating of Commercial Acrylic Sheet with n-heptylamine polymer after
argon plasma cleaning**

30 Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an

argon plasma under the following conditions:

0.50 Torr pressure
200 kHz frequency
10 Watt load power
60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-heptylamine vapour under the following conditions:

0.40 Torr pressure
200 kHz frequency
20 Watt load power
180 second duration.

A coating of plasma polymer ca 110 nm thick formed.

EXAMPLE 5 - Coating of Commercial Acrylic Sheet with n-hexane polymer after air plasma cleaning

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

0.50 Torr pressure
200 kHz frequency
10 Watt load power
60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-hexane vapour under the following conditions:

0.11 Torr pressure
200 kHz frequency
20 Watt load power
120 second duration.

5

A coating of plasma polymer ca 140 nm thick formed.

EXAMPLE 6 Coating of commercial acrylic sheet with n-hexane polymer after argon plasma cleaning

10

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet. Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an argon plasma under the following conditions:

15

0.50 Torr pressure
200 kHz frequency
10 Watt load power
60 second duration.

20

The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-hexane vapour under the following conditions:

25

0.40 Torr pressure
200 kHz frequency
20 Watt load power
120 second duration.

30

A coating of plasma polymer ca 130 nm thick formed.

EXAMPLE 7 - Coating of commercial acrylic sheet with methanol polymer after air plasma cleaning

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.

- 5 Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

10 0.50 Torr pressure
 200 kHz frequency
 10 Watt load power
 60 second duration.

- 15 The coating was applied to the plasma-cleaned sample by exposure to a plasma in methanol vapour under the following conditions:

 0.60 Torr pressure
 200 kHz frequency
 20 Watt load power
20 600 second duration.

A coating of plasma polymer ca 51 nm thick formed.

EXAMPLE 8 Coating of commercial acrylic sheet with perfluorodimethylcyclohexane polymer after air plasma cleaning

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.
5 Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

10 0.50 Torr pressure
200 kHz frequency
10 Watt load power
60 second duration.

The coating was applied to the plasma-cleaned sample by exposure to a plasma in
15 perfluorodimethylcyclohexane vapour under the following conditions:

0.2 Torr pressure
200 kHz frequency
5 Watt load power
20 180 second duration.

A coating of plasma polymer ca 120 nm thick formed.

**EXAMPLE 9 - Coating of commercial acrylic sheet with methyl methacrylate polymer
25 after air plasma cleaning**

Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.
Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an
30 air plasma under the following conditions:

0.50 Torr pressure

200 kHz frequency
10 Watt load power
60 second duration.

- 5 The coating was applied to the plasma-cleaned sample by exposure to a plasma in methyl methacrylate vapour under the following conditions:

 0.5 Torr pressure
 200 kHz frequency
10 10 Watt load power
 60 second duration.

A coating of plasma polymer ca 210 nm thick formed.

15

EXAMPLE 10 - Coating of commercial acrylic sheet with n-butyl methacrylate polymer after air plasma cleaning

- Test strips of 35 cm x 3 cm were cut from 3 mm thick commercial cast acrylic sheet.
20 Each strip was cleaned by wiping with toluene-soaked, lint-free tissues, and wiping repeated twice more with fresh tissues. Final preparation of the surface was achieved by treatment in an air plasma under the following conditions:

 0.50 Torr pressure
25 200 kHz frequency
 10 Watt load power
 60 second duration.

- The coating was applied to the plasma-cleaned sample by exposure to a plasma in n-butyl
30 methacrylate vapour under the following conditions:

 0.5 Torr pressure

200 kHz frequency

5 Watt load power

120 second duration.

5 A coating of plasma polymer ca 125 nm thick formed.

EXAMPLE 11 - Evaluation of effect of coatings on craze resistance to polar materials.

10 Test strips prepared according to Examples 3 - 10 were tested for susceptibility to crazing using a modification of the cantilever test method of Example 2. The samples were 35 cm long and a weight of 1 kg was suspended from the unsupported end of the test strip. The load was applied and the test fluid (isopropanol) applied immediately to the tensile surface which was kept wet and under observation until crazing occurred.

15 Although all test strips eventually crazed, all treated strips lasted at least ten times longer than uncoated control strips.

These results demonstrate that the process of the invention enhances the craze resistance
20 of commercial acrylic sheet such as that used for glazing or signs as well as the stretched acrylic sheet used for aircraft windows.

Throughout this specification, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the
25 inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

CLAIMS

1. A method for reducing crazing in a plastics material characterised in that it comprises the steps of:
 - 5 (1) cleaning the surface of the material; and
 - (2) exposing the cleaned surface to plasma of a monomer vapour so as to produce a substantially non-oxidising plasma polymer coating on the surface.
2. A method as claimed in Claim 1, characterised in that the monomer in step (2) is a
10 saturated or unsaturated organic compound capable of producing a coating of a substantially non-oxidising polymer containing organic groups.
3. A method as claimed in Claim 2, characterised in that the monomer is a saturated
15 monomer selected from the group consisting of siloxanes, fluorinated compounds, lower hydrocarbons, lower alcohols, lower alkylamines and mixtures thereof.
4. A method as claimed in Claim 2, characterised in that the monomer is an unsaturated
20 monomer selected from the group consisting of acrylic esters, methacrylic esters, vinyl esters, vinyl aromatics, unsaturated or polyunsaturated hydrocarbons and mixtures thereof.
5. A method as claimed in Claim 4, characterised in that the monomer is selected from the
group consisting of methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate,
methyl methacrylate, ethyl methacrylate, *n*-butyl methacrylate, 2-ethylhexyl methacrylate,
25 vinyl acetate, styrene, *p*-chloromethylstyrene, 2-vinylpyridine, 4-vinylpyridine, N-vinylpyrrolidone, vinyl halides of the formula $\text{CH}_2=\text{CHX}$ wherein X is Cl or F, vinylidene
halides of the formula $\text{CH}_2=\text{CX}_2$ wherein X is independently Cl or F, vinyl ethers of the
formula $\text{CH}_2=\text{CHOR}$ wherein R is alkyl, and allyl derivatives such as allyl ethers, allyl
carbonates or diallyl carbonates.
30
6. A method as claimed in Claim 1 or Claim 2, characterised in that the plastics material is
an acrylic polymer and the polymer coating is a siloxane or perfluorinated compound.

7. A method as claimed in Claim 6, characterised in that the polymer is produced from a monomer selected from the group consisting of hexamethyldisiloxane, vinyltrimethoxysilane, perfluorocyclohexane and tetrafluoroethylene.
- 5 8. A method as claimed in Claim 1 or Claim 2, characterised in that the plastics material is to be used in an environment where it is exposed to hydrophobic molecules and the polymer coating is a hydrophilic coating.
9. A method as claimed in Claim 8, characterised in that the polymer is produced from a
10 monomer produced from an alcohol or alkylamine.
10. A method as claimed in Claim 9, characterised in that the polymer is produced from an alcohol selected from the group consisting of methanol, ethanol and the various isomers of propanol or butanol.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00101

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C08F 2/52 C08J 7/04 7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F 2/52 C08J 7/04 7/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT: (CRAZ: OR CRACK:) and (PLASMA or ION: or DISCHARG:) and IPC as above

JAPIO: as above for WPAT CASM: (CRAZ: or CRACK:) and PLASMA and PLASTIC:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91/16378 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 31 October 1991 Entire document	1-10
A	AU 73964/91 A (THE GOODYEAR TIRE & RUBBER COMPANY) 3 October 1991 Entire document	1-10

☒ Further documents are listed in the continuation of Box C

☒ See patent family annex

<p>* Special categories of cited documents:</p>		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
9 April 1997

Date of mailing of the international search report
23 APR 1997

Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA Facsimile No.: (06) 285 3929

Authorized officer
N.L. KING
Telephone No.: (06) 283 2150

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 97/00101

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 89/11500 A (COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION) 30 November 1989 Entire document	1-10
A, P	US 5494712 A (ING-FENG HU et al) 27 February 1996 Entire document	1-10
A	EP 176636 A1 (JAPAN SYNTHETIC RUBBER CO. LTD) 9 April 1986 Entire document	1-10
A	JP 02022339 A (HITACHI CABLE KK) 25 January 1990 Derwent Abstract Accession No 90-070437 Abstract	1-10
A	JP 58008517 A (SUMITOMO DENKI KOGYO KK) 18 January 1983 Abstract	1-10

Information on patent family members

PCT/AU 97/00101

三、

END OF ANNEX